Lecture on First-principles Computation (4): Particles moving in a Periodic Potential – the Band Theory

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Electrons moving in a periodic potential

$$\frac{1}{2}\sum_{i\neq j}^{N}\frac{1}{|\boldsymbol{r}_i-\boldsymbol{r}_j|}+\sum_{i=1}^{N}v_{ext}(\boldsymbol{r}_i) \longrightarrow \sum_{i=1}^{N}V_{eff}(\boldsymbol{r}_i)$$

(e.g., under the Hartree-Fock approximation)

$$\hat{H}=\sum_{i=1}^{N}\left[-\frac{\nabla_i^2}{2\mathrm{m}}+V_{eff}(\mathbf{r_i})\right]$$

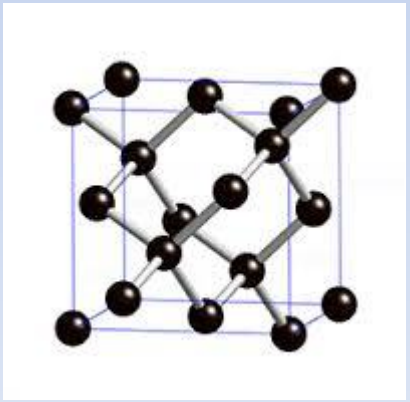
Consider crystalline solids:

$$V_{eff}(\boldsymbol{r})=V_{eff}(\boldsymbol{r}+\boldsymbol{R})$$

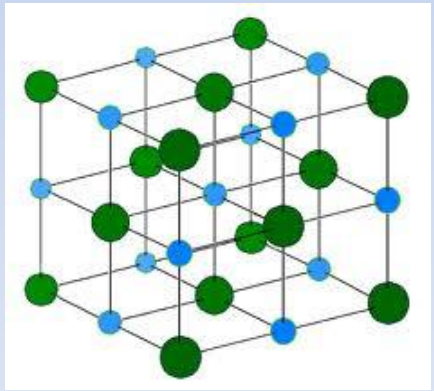
$\mathbf{R}=n_1\mathbf{a_1}+n_2\mathbf{a_2}+n_3\mathbf{a_3}, \quad n_1,n_2,n_3\in I$ (integer numbers)

Bravais Lattice

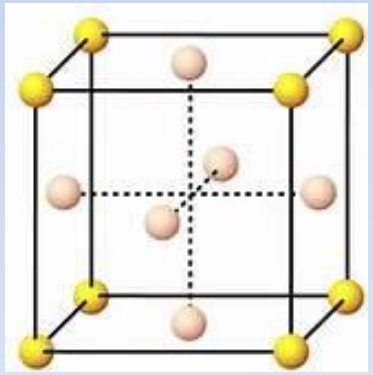
- Bravais lattice is a collection of infinitely many discrete lattice points, which has the property that the lattice looks exactly the same regardless the reference point.
- Crystal structure = unit cell + Bravais lattice
- There are 14 Bravais lattice in 3D; the complexity of crystals stems from the complexity of the unit cell.



Diamond
(Zinc Blende)

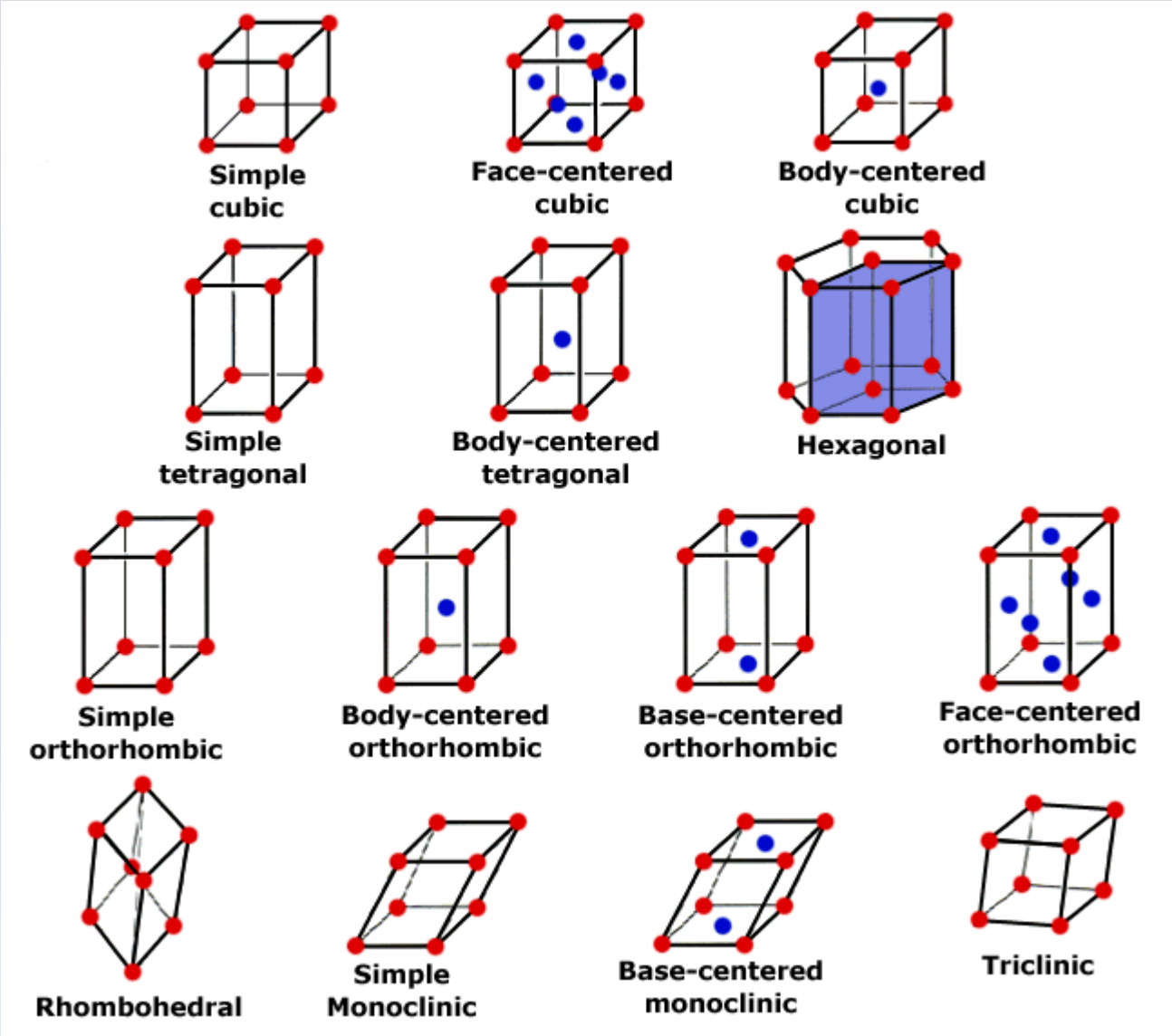


NaCl



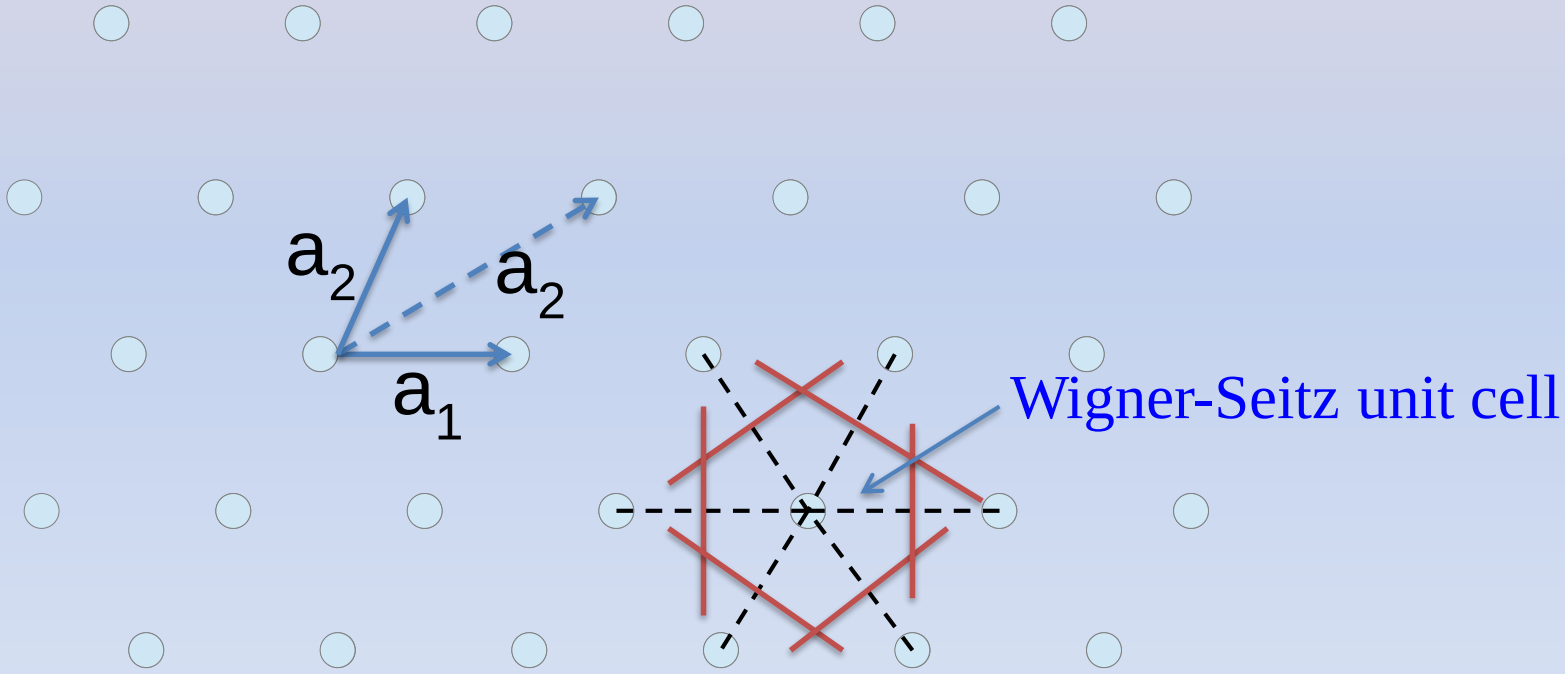
Face-Centered Cubic (fcc)

Fourteen Bravais lattice (3D)



Primitive unit cell, Wigner-Seitz cell

The way to choose the unit cell is not unique, but some particular choice can reflect the symmetry of the lattice.



Any spatial point within the Wigner-Seitz (WS) cell associated with a particular lattice point should have a smaller distance to this lattice point than to any other lattice point.

The reciprocal lattice

Basis vectors in the reciprocal space

$$\mathbf{b}_1 = \frac{2\pi}{\Omega}\mathbf{a}_2 \times \mathbf{a}_3$$

$$\mathbf{b}_2 = \frac{2\pi}{\Omega}\mathbf{a}_3 \times \mathbf{a}_1$$

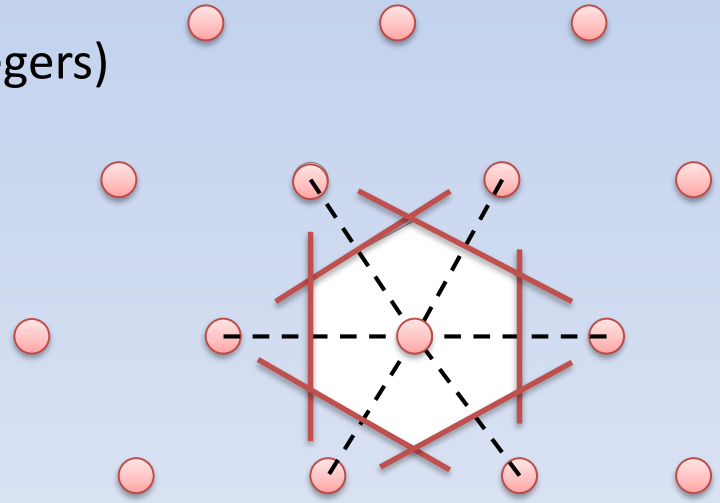
$$\mathbf{b}_3 = \frac{2\pi}{\Omega}\mathbf{a}_1 \times \mathbf{a}_2$$

$$\Omega = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$$

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$$

Reciprocal lattice vectors (n_1, n_2, n_3 are integers)

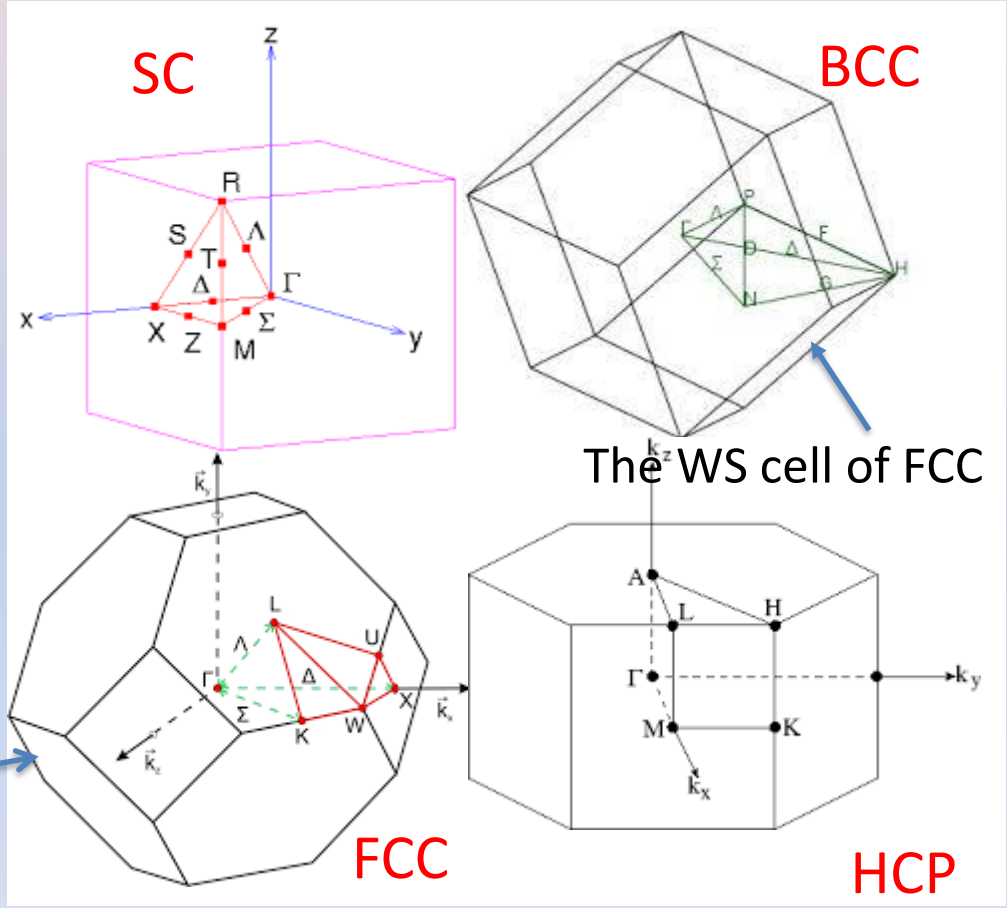
$$\mathbf{G} = n_1\mathbf{b}_1 + n_2\mathbf{b}_2 + n_3\mathbf{b}_3$$



First Brillouin zone (BZ): the Wigner-Seitz cell in the reciprocal space.

The 1st Brillouin zone (BZ)

The reciprocal lattice of FCC is BCC, and *vice versa*.



Γ, L, X, W, Δ, K, Q, Λ, Σ, M, Z, … are high-symmetry point in the BZ. (The name comes form the representation of the corresponding symmetry groups)

Electrons in a periodic potential: the Bloch theorem

$$\hat{H} = \sum_{i=1}^{N} \hat{h}(i) = \sum_{i=1}^{N} \left[-\frac{\nabla_i^2}{2\mathrm{m}} + V_{eff}(\boldsymbol{r}_\mathbf{i}) \right]$$

$$\hat{h} = -\frac{\nabla^2}{2\mathrm{m}} + V_{eff}(\boldsymbol{r}), \qquad V_{eff}(\mathbf{r}) = V_{eff}(\boldsymbol{r} + \boldsymbol{R})$$

$$\hat{h}\psi_l(\mathbf{r}) = \epsilon_l \psi_l(\mathbf{r})$$

Generalized Born-von Karman (BvK) boundary condition:

$$\psi_l(\boldsymbol{r} + L_1\mathbf{a_1}) = \psi_l(\boldsymbol{r})$$
$$\psi_l(\boldsymbol{r} + L_2\mathbf{a_2}) = \psi_l(\boldsymbol{r})$$
$$\psi_l(\boldsymbol{r} + L_3\mathbf{a_3}) = \psi_l(\boldsymbol{r})$$

Total number of unit cells:

$$L = L_1 L_2 L_3$$

Electrons in a periodic potential: the Bloch Theorem

$$\hat{h} = -\frac{\nabla^2}{2\mathrm{m}} + V_{eff}(\boldsymbol{r}), \quad V_{eff}(\boldsymbol{r}) = V_{eff}(\boldsymbol{r}+\boldsymbol{R})$$

$$\hat{T}_{\boldsymbol{R}}\hat{h} = \hat{h}\hat{T}_{\boldsymbol{R}}, \qquad \hat{T}_{\boldsymbol{R}}\psi(\boldsymbol{r}) = \psi(\boldsymbol{r}+\boldsymbol{R})$$

$$\hat{h}(\boldsymbol{r})\psi_l(\boldsymbol{r}) = \epsilon_l\psi_l(\boldsymbol{r})$$

The Bloch theorem

$$\psi_l(\boldsymbol{r}+\boldsymbol{R}) = e^{i\boldsymbol{k}\cdot\boldsymbol{R}}\psi_l(\boldsymbol{r}), \qquad \psi_l(\boldsymbol{r}) \rightarrow \psi_{n\boldsymbol{k}}(\boldsymbol{r})$$

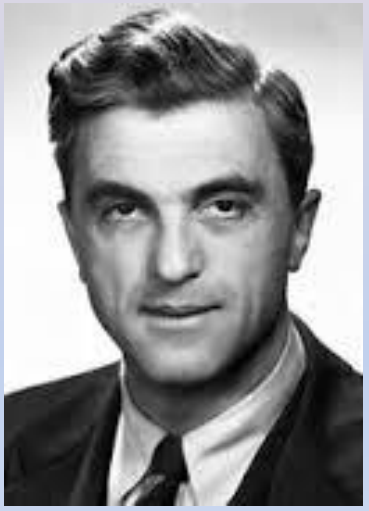
or

$$\psi_{n\boldsymbol{k}}(\mathbf{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}u_{n\boldsymbol{k}}(\boldsymbol{r}), \qquad u_{n\boldsymbol{k}}(\boldsymbol{r}+\boldsymbol{R}) = u_{n\boldsymbol{k}}(\boldsymbol{r})$$

The Bloch theorem

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}), \qquad u_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$$

$$\left.\begin{aligned} e^{iL_j\mathbf{k}\cdot\mathbf{a_j}} &= 1 \\ \boldsymbol{k} &= \sum_{j=1}^{3} k_j\,\mathbf{b_j} \end{aligned}\right\} \longrightarrow \quad k_j = \frac{n_j}{L_j}, n_j \in I$$



Felix Bloch

The label ***k*** is usually restricted within the 1st BZ.

$\psi_{n\boldsymbol{k}}(\boldsymbol{r})$ are called Bloch orbitals, and the electrons moving in a periodic potential are often called Bloch electrons.

Solving the Bloch equation

If $V_{eff}(\boldsymbol{r}) = V(\boldsymbol{r})$ changes slowly in space, the Bloch orbitals can be expanded in terms of plane waves.

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{n\mathbf{k}+\mathbf{G}}\, e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

$$V(\boldsymbol{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\boldsymbol{G}\cdot\boldsymbol{r}}, \qquad V_{\mathbf{G}} = \frac{1}{\Omega} \int_{cell} d\,\boldsymbol{r} e^{-i\boldsymbol{G}\cdot\boldsymbol{r}} V(\boldsymbol{r})$$

$$(\hat{h} - \epsilon)\psi_{n\mathbf{k}}(\mathbf{r}) = \left(-\frac{\nabla^2}{2\mathrm{m}} + V(\mathbf{r}) - \epsilon\right)\psi_{n\mathbf{k}}(\mathbf{r}) = 0 \quad \Rightarrow$$

$$\sum_{\mathbf{G}} \left[\left(\frac{|\,\mathbf{k}+\mathbf{G}\,|^2}{2\mathrm{m}} - \epsilon\right) c_{n\mathbf{k}+\mathbf{G}} + \sum_{\mathbf{G}'} V_{\mathbf{G}-\mathbf{G}'}\, c_{n\mathbf{k}+\mathbf{G}'}\right] e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} = 0$$

Solving the Bloch equation

We obtain the following secular equation (can be viewed as the representation of the Bloch equation in the reciprocal space)

$$\left(\frac{|\,\mathbf{k}+\mathbf{G}\,|^2}{2\mathrm{m}}-\epsilon\right)c_{n\mathbf{k}+\mathbf{G}}+\sum_{\mathbf{G}'}V_{\mathbf{G}-\mathbf{G}'}\,c_{n\mathbf{k}+\mathbf{G}'}=0$$

$$\begin{pmatrix} \frac{|\,\mathbf{k}+\mathbf{G}\,|^2}{2\mathrm{m}} & V_{\mathbf{G}-\mathbf{G}_1} & V_{\mathbf{G}-\mathbf{G}_2} & \cdots \\ V_{\mathbf{G}_1-\mathbf{G}} & \frac{|\,\mathbf{k}+\mathbf{G}_1\,|^2}{2\mathrm{m}} & V_{\mathbf{G}_1-\mathbf{G}_2} & \cdots \\ V_{\mathbf{G}_2-\mathbf{G}} & V_{\mathbf{G}_2-\mathbf{G}_1} & \frac{|\,\mathbf{k}+\mathbf{G}_2\,|^2}{2\mathrm{m}} & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{pmatrix} \begin{pmatrix} c_{n+\mathbf{G}} \\ c_{n\mathbf{k}+\mathbf{G}_1} \\ c_{n\mathbf{k}+\mathbf{G}_2} \\ \cdots \end{pmatrix} = \epsilon \begin{pmatrix} c_{n\mathbf{k}+\mathbf{G}} \\ c_{n+\mathbf{G}_1} \\ c_{n\mathbf{k}+\mathbf{G}_2} \\ \cdots \end{pmatrix}$$

Consider the non-degenerate case ...

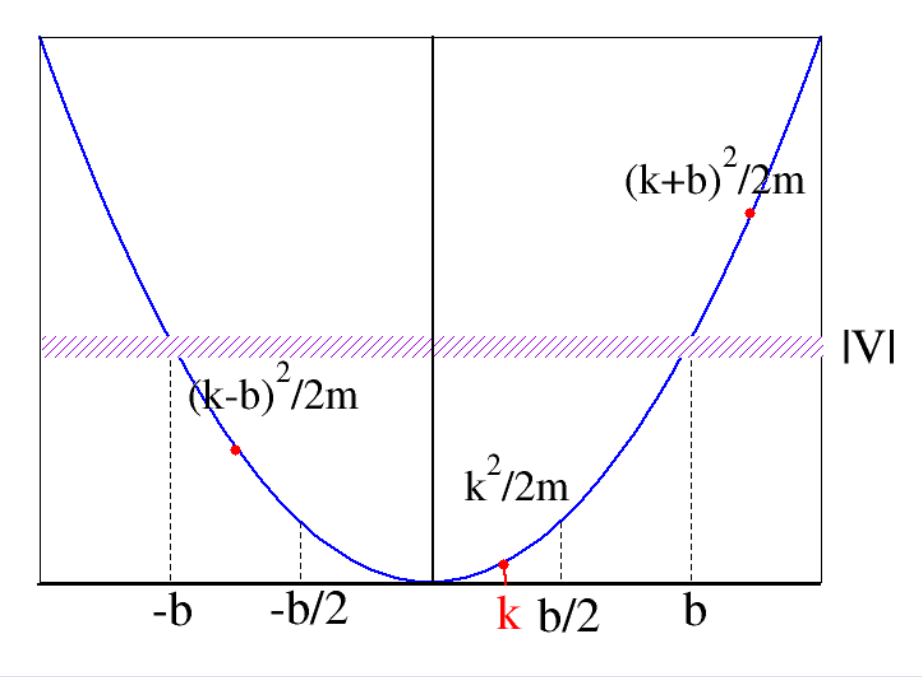
$$\left(\frac{(\boldsymbol{k}+\boldsymbol{G})^2}{2\mathrm{m}}-\epsilon\right)c_{n\boldsymbol{k}+\boldsymbol{G}}+\sum_{\boldsymbol{G}'}V_{\boldsymbol{G}-\boldsymbol{G}'}\,c_{n\boldsymbol{k}+\boldsymbol{G}'}=0$$

Assume: $V_{\boldsymbol{G}=0}=0$ and

$$\left|\frac{|\,\boldsymbol{k}+\boldsymbol{G}\,|^2}{2\mathrm{m}}-\frac{|\,\boldsymbol{k}+\boldsymbol{G}'\,|^2}{2\mathrm{m}}\right| \gg |\,V_{\boldsymbol{G}''}\,|$$

for any $\boldsymbol{G}\neq\boldsymbol{G}'$,

$$\epsilon \approx \frac{|\,\boldsymbol{k}+\boldsymbol{G}\,|^2}{2\mathrm{m}}+\sum_{\boldsymbol{G}'\neq\boldsymbol{G}}\frac{|\,V_{\boldsymbol{G}-\boldsymbol{G}'}\,|^2}{\epsilon^0_{\boldsymbol{k}+\boldsymbol{G}}-\epsilon^0_{\boldsymbol{k}+\boldsymbol{G}'}}$$



$$\epsilon^0_{\boldsymbol{k}+\boldsymbol{G}}=|\,\boldsymbol{k}+\boldsymbol{G}\,|^2/2\mathrm{m} \quad\Rightarrow\quad \epsilon_{n\boldsymbol{k}}\approx\epsilon^0_{\boldsymbol{k}+\boldsymbol{G}}$$

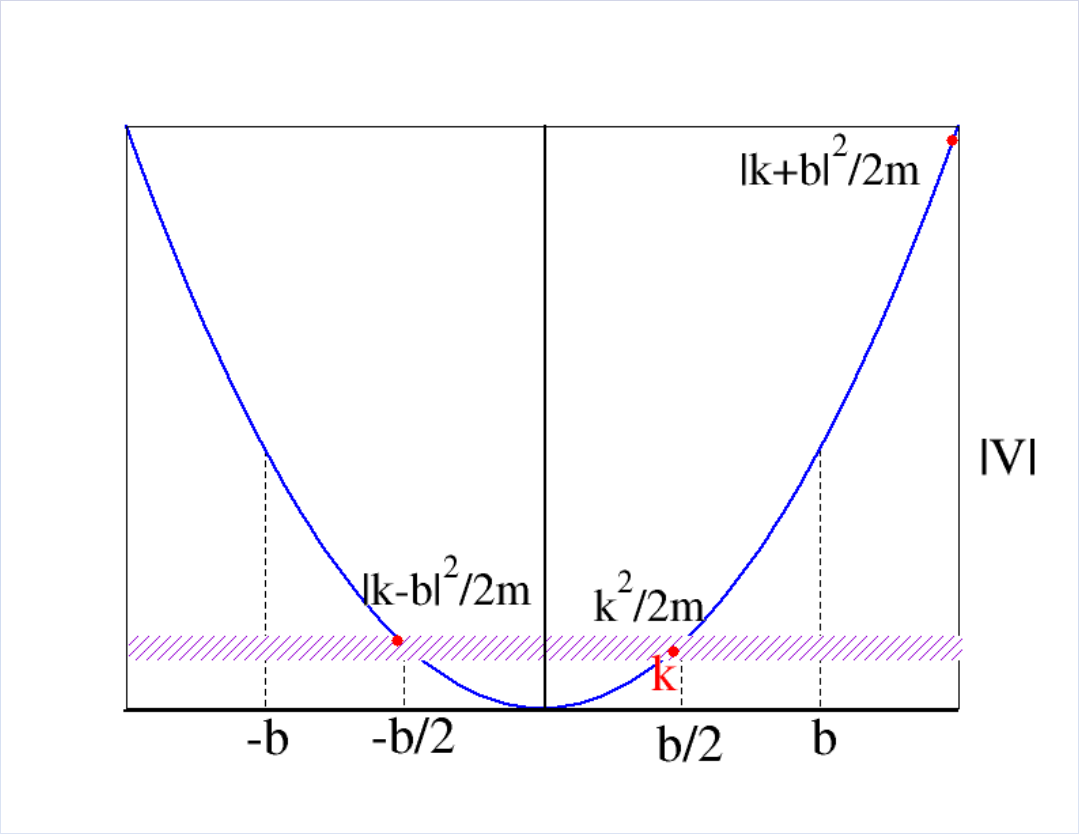
The degenerate case

$$\frac{|\boldsymbol{k}+\boldsymbol{G}|^2}{2\mathrm{m}} \approx \frac{|\boldsymbol{k}+\boldsymbol{G}'|^2}{2\mathrm{m}} = \epsilon^0_{\boldsymbol{k}+\boldsymbol{G}} \qquad V_{\boldsymbol{G}-\boldsymbol{G}'} = V$$

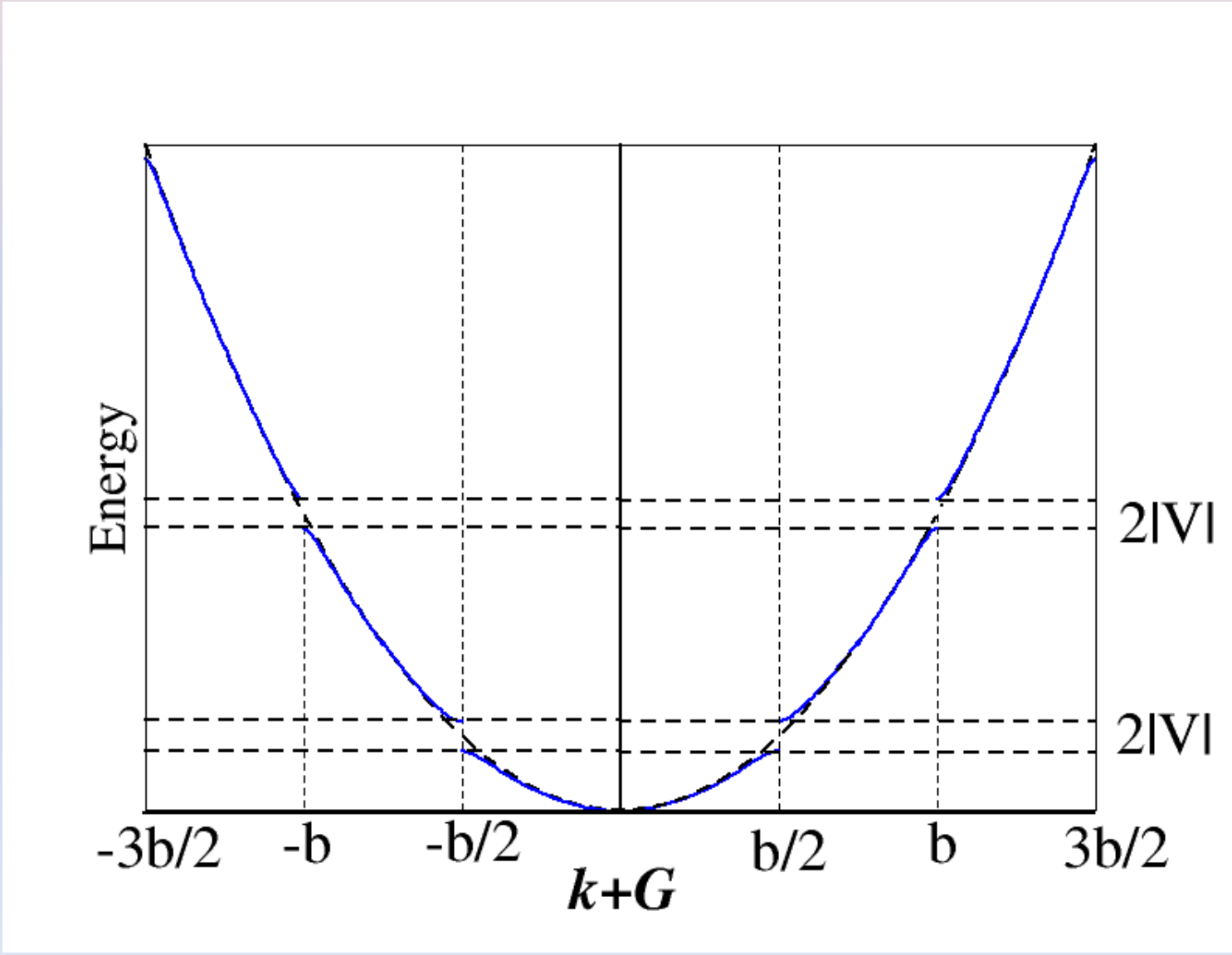
$$\begin{vmatrix} \frac{|\boldsymbol{k}+\boldsymbol{G}|^2}{2m} - \epsilon & V \\ V^* & \frac{|\boldsymbol{k}+\boldsymbol{G}'|^2}{2m} - \epsilon \end{vmatrix} = 0$$

$$\epsilon_+ \approx \frac{|\boldsymbol{k}+\boldsymbol{G}|^2}{2m} + |V|$$

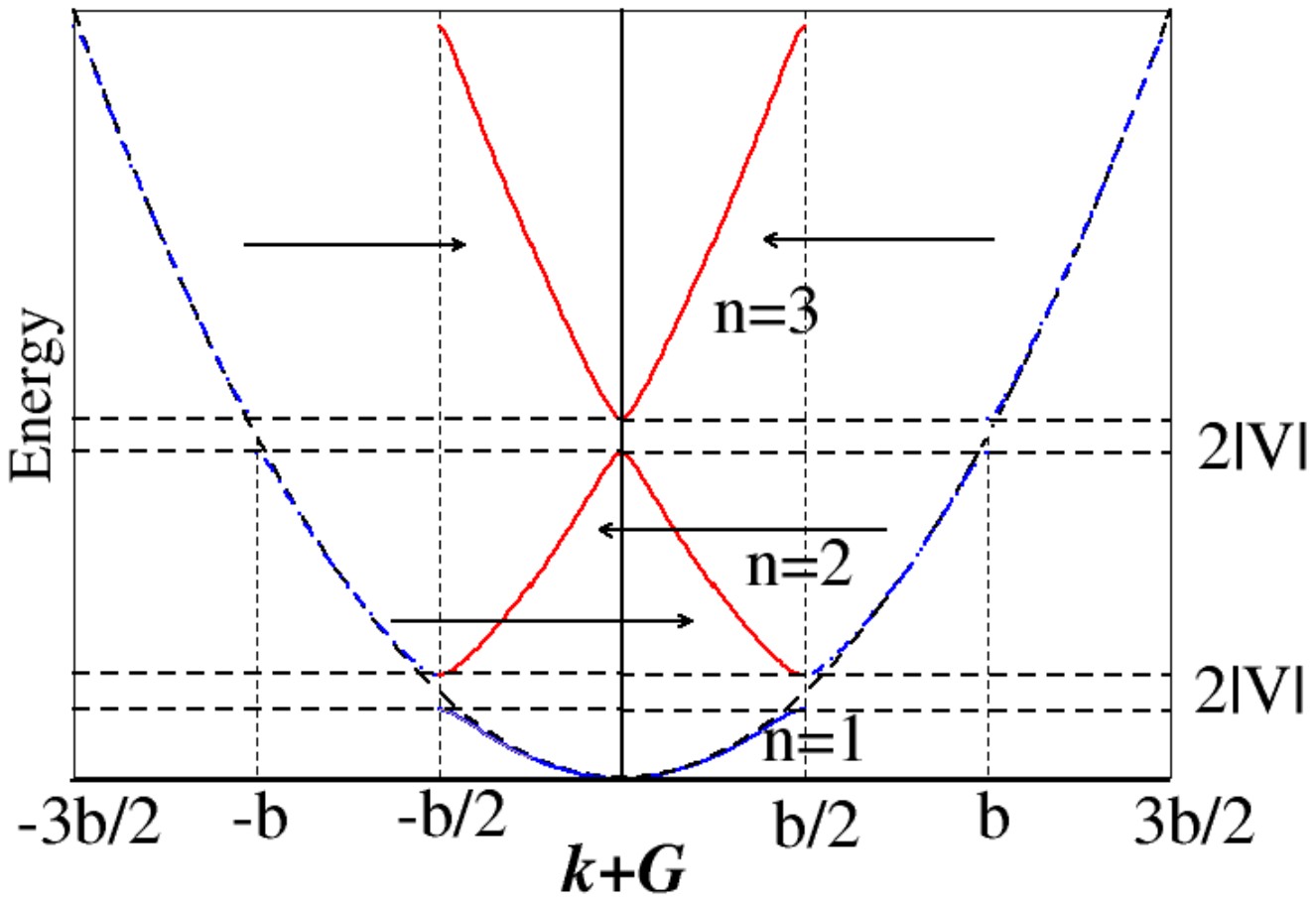
$$\epsilon_- \approx \frac{|\boldsymbol{k}+\boldsymbol{G}|^2}{2m} - |V|$$



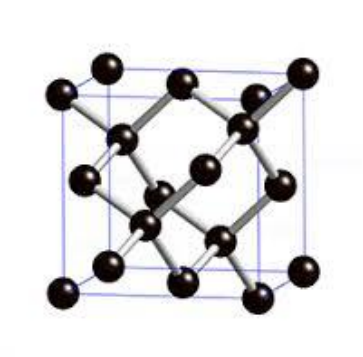
Single-particle energy level in a periodic potential



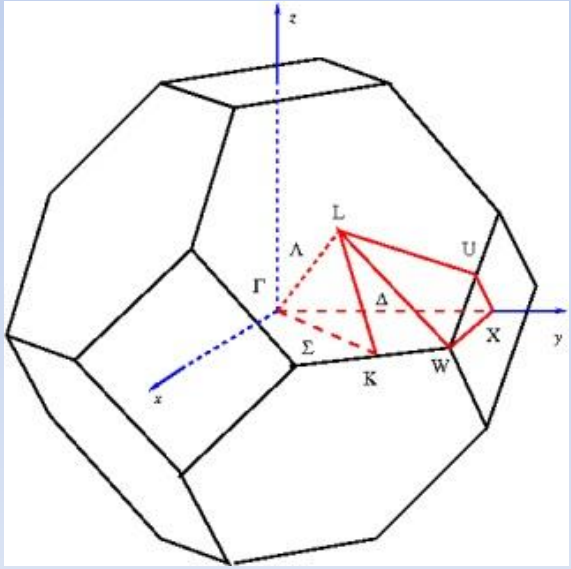
The formation of bands



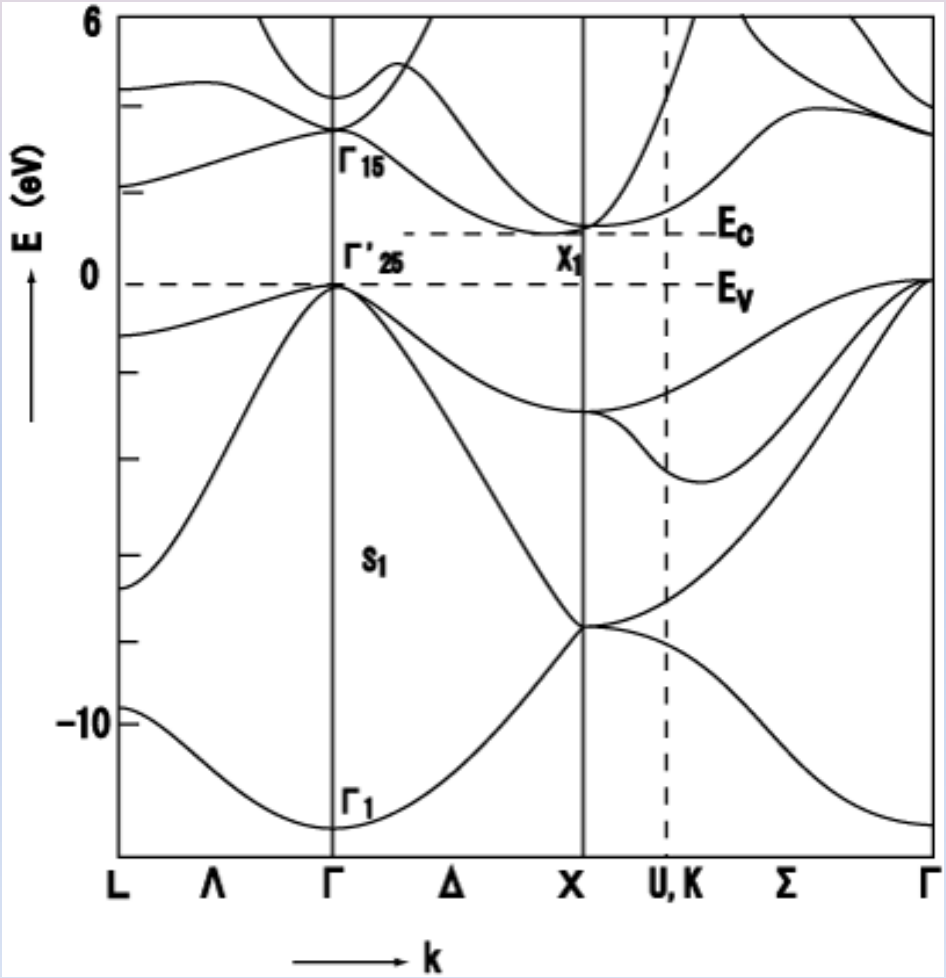
Energy bands in real solid (silicon)



Silicon crystal structure

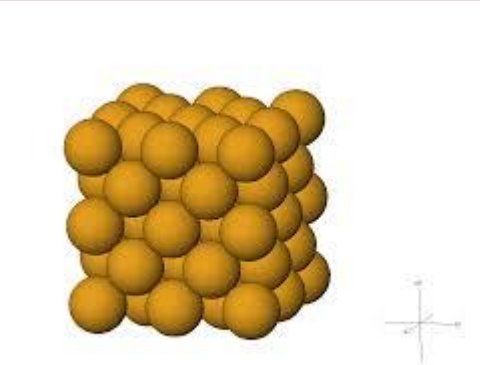


Brillouin zone

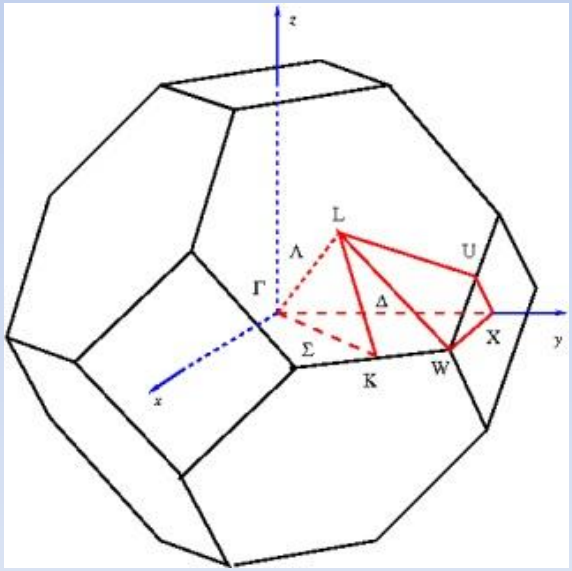


Si band structure

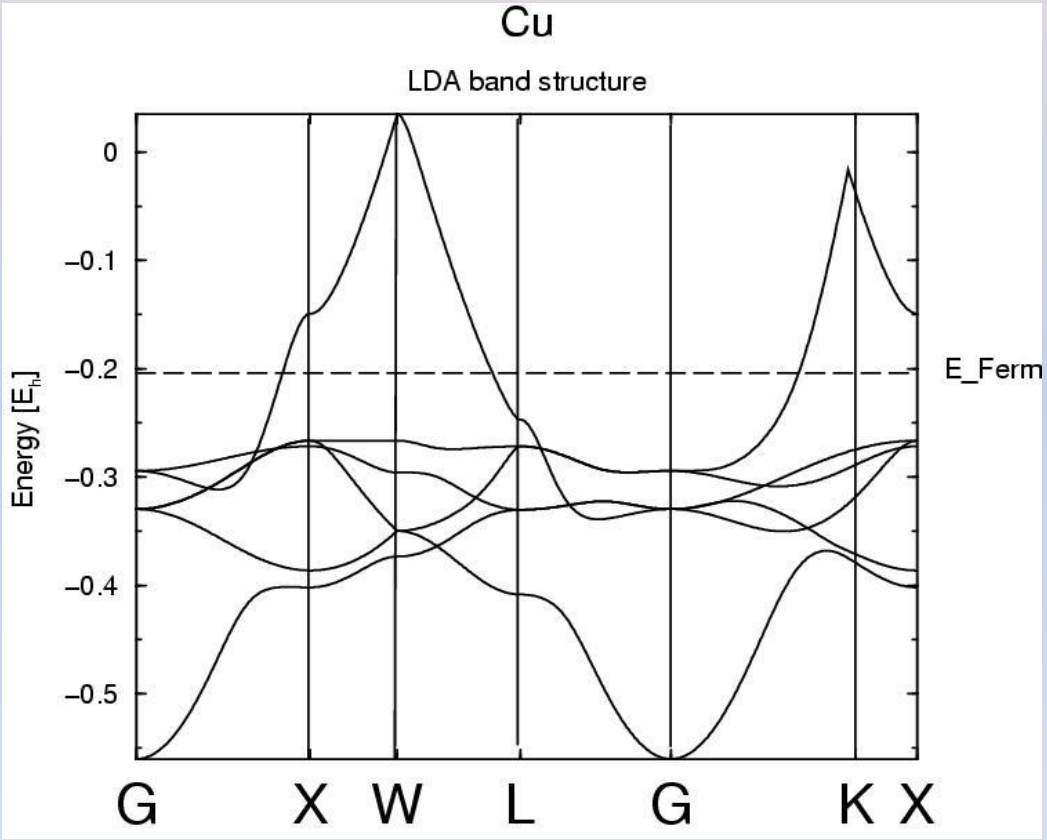
The band structure of copper



copper crystal structure



Brillouin zone



Band structure of copper

Density of states (DOS)

$D(E)dE$: number of electronic states within the energy window between E and $E + dE$.

$$\int_{E_1}^{E_2} D(E)dE = \sum_{\substack{n,\boldsymbol{k} \\ E_1 \le \epsilon_{n\boldsymbol{k}} \le E_2}} (1) \approx \frac{V}{(2\pi)^3} \sum_{\substack{n \\ E_1 \le \epsilon_{n\boldsymbol{k}} \le E_2}} \int (d^3k)$$

$$= \frac{V}{(2\pi)^3} \sum_{\substack{n \\ E_1 \le \epsilon_{n\boldsymbol{k}} \le E_2}} \int \frac{d^3k}{dE} dE = \sum_n \int_{E_1}^{E_2} dE \int_{\epsilon_{n\boldsymbol{k}}=E} \frac{d^2k}{|\nabla_{\boldsymbol{k}} \epsilon_{n\boldsymbol{k}}|}$$

Area of 2D cross section

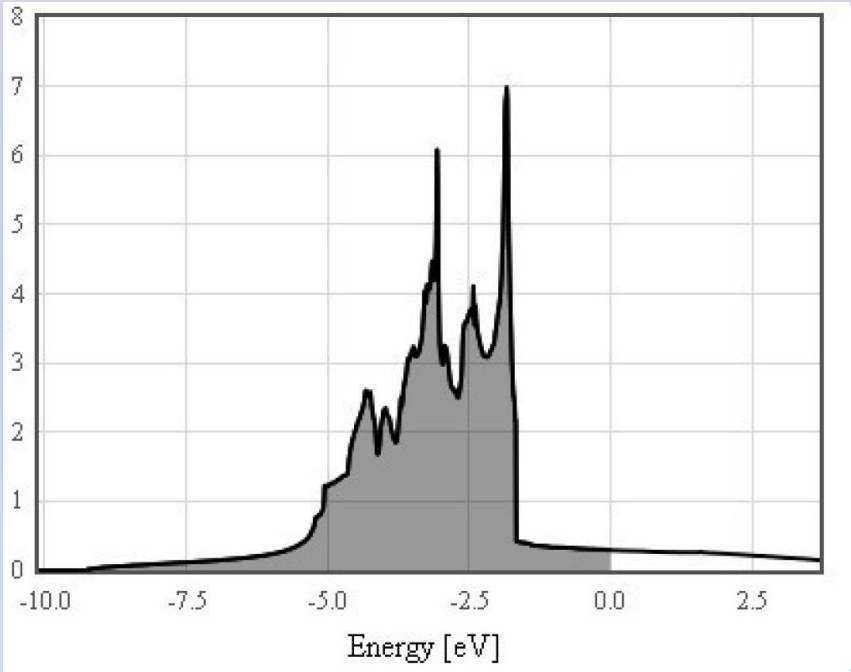
For a 3D system:

$$D(E) = \sum_{n,\boldsymbol{k}} \delta(E - \epsilon_{n\boldsymbol{k}}) = \sum_n \int_{E=\epsilon_{n\boldsymbol{k}}} d^2k \frac{1}{|\nabla_{\boldsymbol{k}} \epsilon_{n\boldsymbol{k}}|}$$

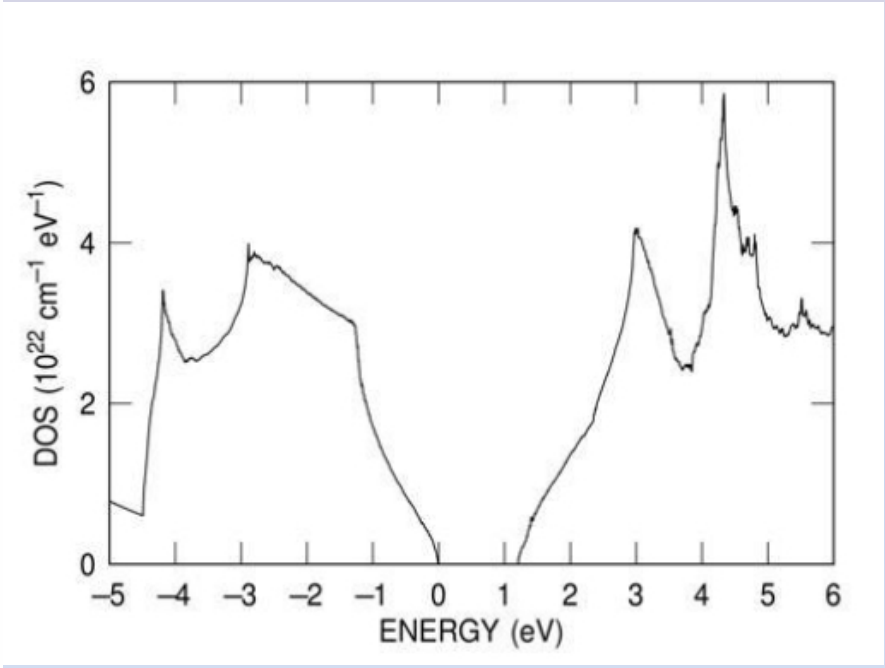
Integration over a 2D energy isosurface

DOS of real materials

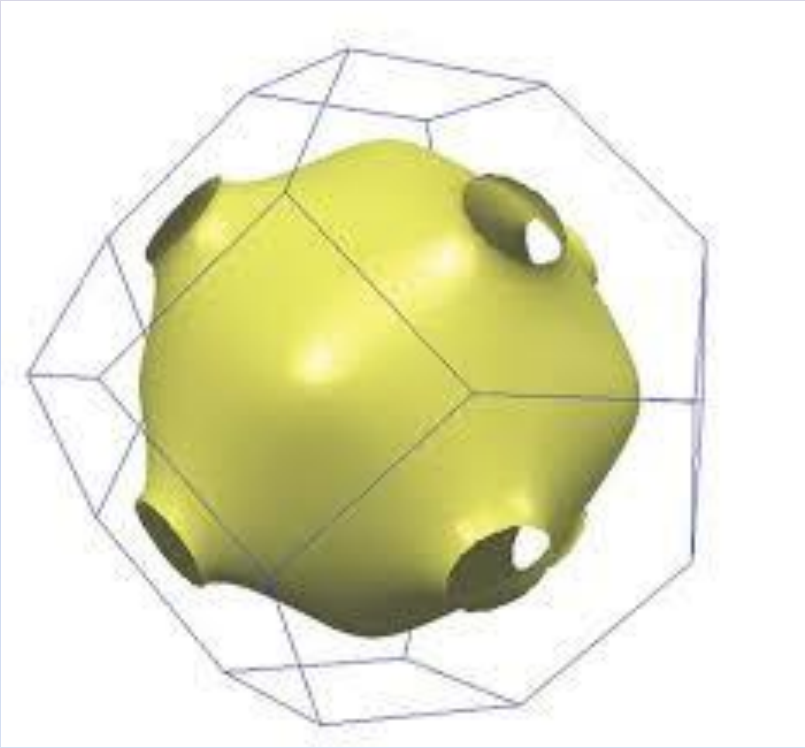
Copper



Silicon



Fermi surface of copper



Summary

$$\left(\frac{|\,\boldsymbol{k}+\boldsymbol{G}\,|^2}{2m}-\epsilon\right)c_{n\boldsymbol{k}+\boldsymbol{G}}+\sum_{\boldsymbol{G}'}V_{\boldsymbol{G}-\boldsymbol{G}'}\,c_{n\boldsymbol{k}+\boldsymbol{G}'}=0$$